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ORGANICS IN ONTARIO DRINKING WATERS

PART I.

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Ontario Ministry of the Environment

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Minister

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Deputy Minister

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ORGANICS IN ONTARIO DRINKING WATERS

PART I.

THE OCCURRENCE AND DETERMINATION OF FREE AND TOTAL POTENTIAL HALOFORMS*

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In 1974 Rook in Holland (1) and Bellar and Litchtenberg (2) in the United States reported that drinking water samples contained chloroform and other haloforms. It was further shown that these substances were not present in the raw water, but formed upon chlorination, the most widely used disinfection process for potable water. The haloforms formed at the highest concentrations were chloroform, bromodichloromethane and chlorodibromomethane.

Since these compounds are potentially toxic, it was considered important to institute a province-wide screening program to determine the extent of the haloform problem in Ontario. After considering the published methods, in view of the possible magnitude of the project, it was decided to investigate the possibility of developing a technique, which could be automated if necessary.

Initial studies indicated that a gas chromatograph equipped with an electron capture detector could be used for direct aqueous injection and that the method could be refined to achieve sensitivities similar to gas stripping methods.

It was shown that the analysis for the target haloforms mentioned before, as well as carbon tetrachloride, trichloroethylene and tetrachloroethylene could be achieved near the 1 ug/l level using 9 ul injection volumes. These limits were similar to those obtained by Bellar and Lichtenberg (2) and Symons and co-workers (3) using the more elaborate gas stripping technique.

Details of the conditions used for the direct aqueous injection method are listed in Figure 1. A scandium tritide electron capture detector supplied by Varian Associates was used. Initially, the column packing used was Chromosorb 101,

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however, later in the study we changed to Tenax since it seemed to give us better peak shapes for carbon tetrachloride. The column is run at two temperatures. At 150°, chloroform, bromodichloromethane, chlorodibromomethane, carbon tetrachloride, trichloroethylene and compounds of similar polarity and volatility are eluted. After raising the temperature to 170° another injection is made, and bromoform and tetrachloroethane are eluted within 10 minutes. Because these higher boiling compounds are seldom found in our samples, the instrument is routinely operated at 150°. Both the injector and detector temperatures were found to be critical since temperatures lower than 250° result in non-linear calibration curves. Further details of the method have been published recently (4).

The direct aqueous injection method is amenable to automation, using commercially available instrumentation. The system we are using is pictured in Figure 2. A Varian model 8000 automatic injector was mounted on the gas chromatograph, which in turn was interfaced with a Spectra-Physics System IV integrator. This set up allows us to analyze up to sixty samples in a 24 hour period. Before putting the direct aqueous injection method on line, it was considered vital that we compare the results we obtained to those given by the published gas stripping procedure (3).

Figure 3 is a schematic presentation of the gas stripping apparatus we are now using. The stripper, which can accommodate a 5 ml sample, is connected to the gas chromatograph and helium supply with a four port valve. The volatile organics are purged from solution and collected on the head of the column which is held at room temperature. After purging

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at 20 ml/minute for 10 minutes, the column oven is heated rapidly to 100°C, and programmed from 100 to 200° at 4°C per minute. The column effluent is detected by a Tracor electrolytic conductivity detector. Detailed conditions for this analysis are shown in Figure 4.

Comparison of standard solutions and spiked raw water samples gave a one to one correlation for these methods.

Figure 5, however, is a graph comparing the two methods for samples from eleven locations run on the same day, and using the same standard solutions for calibration. The linear correlation coefficient was quite good (0.96) but the slope was 0.63.

The first reason we considered for this rather startling difference was purging inefficiency of the gas stripping method. Subsequent studies indicated however that, at 25°C, more than 95% of the chloroform was removed during a 10 minute purge, and 85 to 90% of the bromodichloromethane was removed simultaneously.

Analyses of a number of samples after exhaustive purging yielded the results tabulated in Figure 6. The samples were analyzed by both methods, then 10 ml was purged at 40 ml per minute for 30 minutes, and again analyzed by both methods. It is obvious that the difference in the two methods before purging is equal to the value obtained by the direct aqueous injection method after purging.

A similar result was obtained for bromodichloromethane (see Figure 7). These values were not as significant as those obtained for chloroform, since the error in this region is fairly large.

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It was concluded, after studying this data, that the reason for the difference must be connected with the high injector temperatures used in the direct aqueous injection technique.

To test this hypothesis, a sample of water from Cayuga, Ontario, was sealed in several 15 ml hypo vials containing sodium thiosulphate. The vials were sealed with Teflon-lined septa. Care was taken to ensure that no head space was left in the sealed vials.

The vials were placed in a boiling water bath and, at specified intervals, a vial was removed, cooled to room temperature and analyzed by both methods.

The results are plotted in Figure 8. While the concentration remains fairly constant according to the direct aqueous injection technique, a dramatic increase in the values obtained by the gas stripping method is observed. The increase levels off near the value obtained by the direct injection method.

Figure 9, a plot of the ratio of the two methods shows more clearly that the gas stripping values approach those obtained by direct injection.

A similar plot was obtained for bromodichloromethane (Figure 10).

These results leave us with the conclusion that, when using the direct aqueous injection technique, compounds which are precursors of chloroform and bromodichloromethane decompose at high injector temperatures to produce these haloforms. We therefore can classify results obtained by this method

as the total potential chloroform or bromodichloromethane concentrations. That is, the direct injection technique will produce a value which is the maximum which can be reached while the treated water is in the distribution system.

When the free haloform content of the sample has been determined by the gas stripping technique the total potential haloform result also gives an indication of the amounts of higher molecular weight potentially toxic compounds which are either too soluble or too non-volatile to be detected by the gas stripping technique.

That intermediates of this nature could be detected by the direct injection technique, and not by the purging method was demonstrated by two experiments. In the first a 100 ug/l solution of chloral was analyzed. It was quantitatively converted to chloroform upon direct injection, but no peak was observed using the stripping method.

When the chlorination of aqueous acetone at pH 8 is followed by both techniques the ratio of the two methods is similar to that found when analyzing treated water (see Figure 11).

Lowering the injector temperature to 140^{o} sometimes results in the reduction of the DAI/GS ratio. As yet these results are not consistent.

We therefore propose that results obtained using the gas stripping technique are free haloforms and results obtained using the direct injection technique are the "total potential haloforms".

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ACKNOWLEDGEMENTS.

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The chlorination of acetone was carried out by Dr. W. Bulani and his students at the University of Western Ontario.

The authors are also grateful to Messrs. G. C. Ronan and P. L. Diosady for their interest and encouragement.

References.

1. J. J. Rook, Water Treatment and Examination 23, 234 (1974).

2. T. A. Bellar and J. J. Lichtenberg, J. Am. Water Works Assoc. 703 (1974).

3. J. M. Symons et al, National Organics Reconnaissance Survey for Halogenated Organics in Drinking Water. Water Supply Research Laboratory U.S.E.P.A.

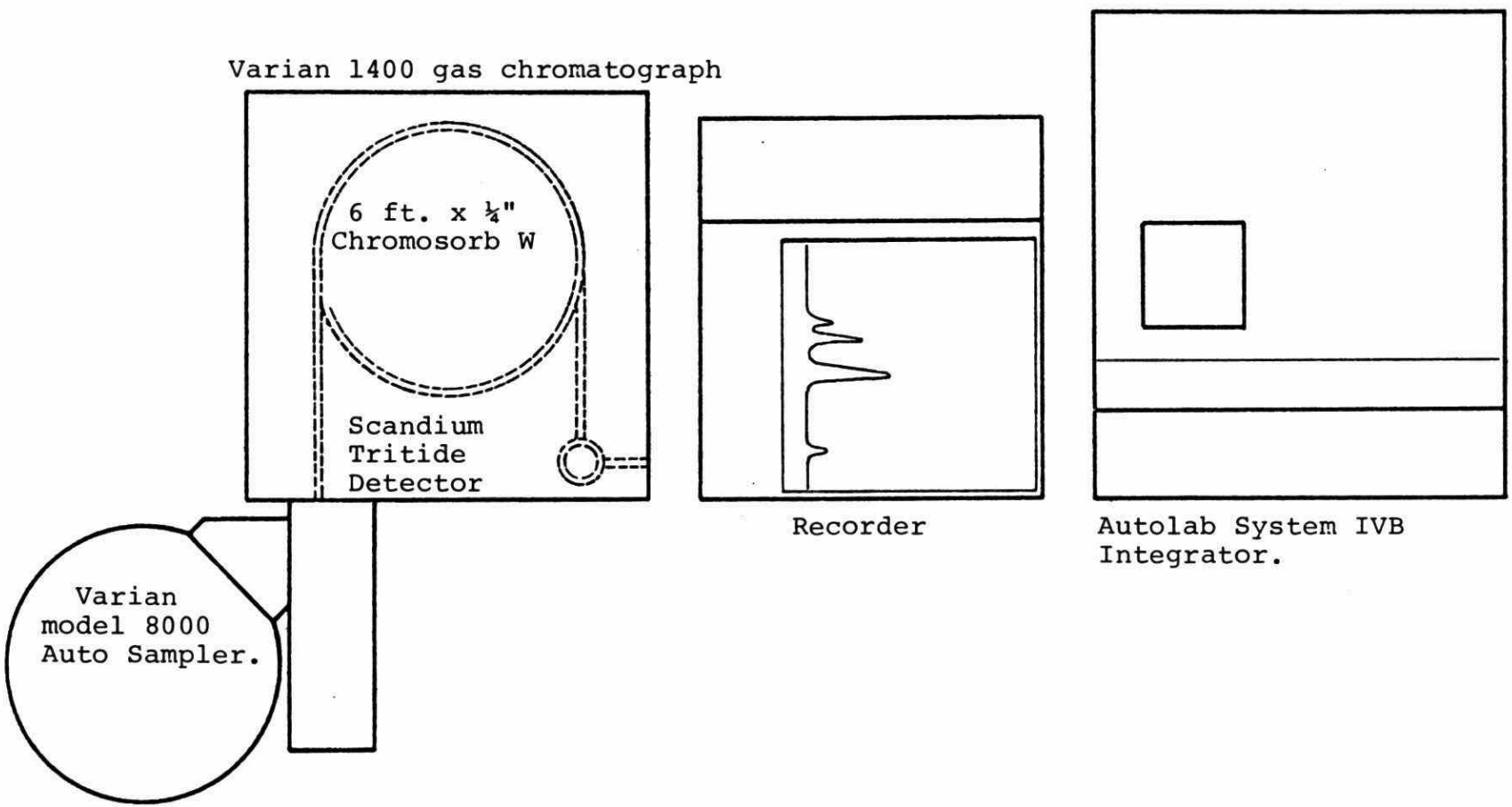
4. A. A. Nicholson and O. Meresz. Bull. of Env. Contamination and Toxicology 14, 453 (1975).

FIGURE 1.

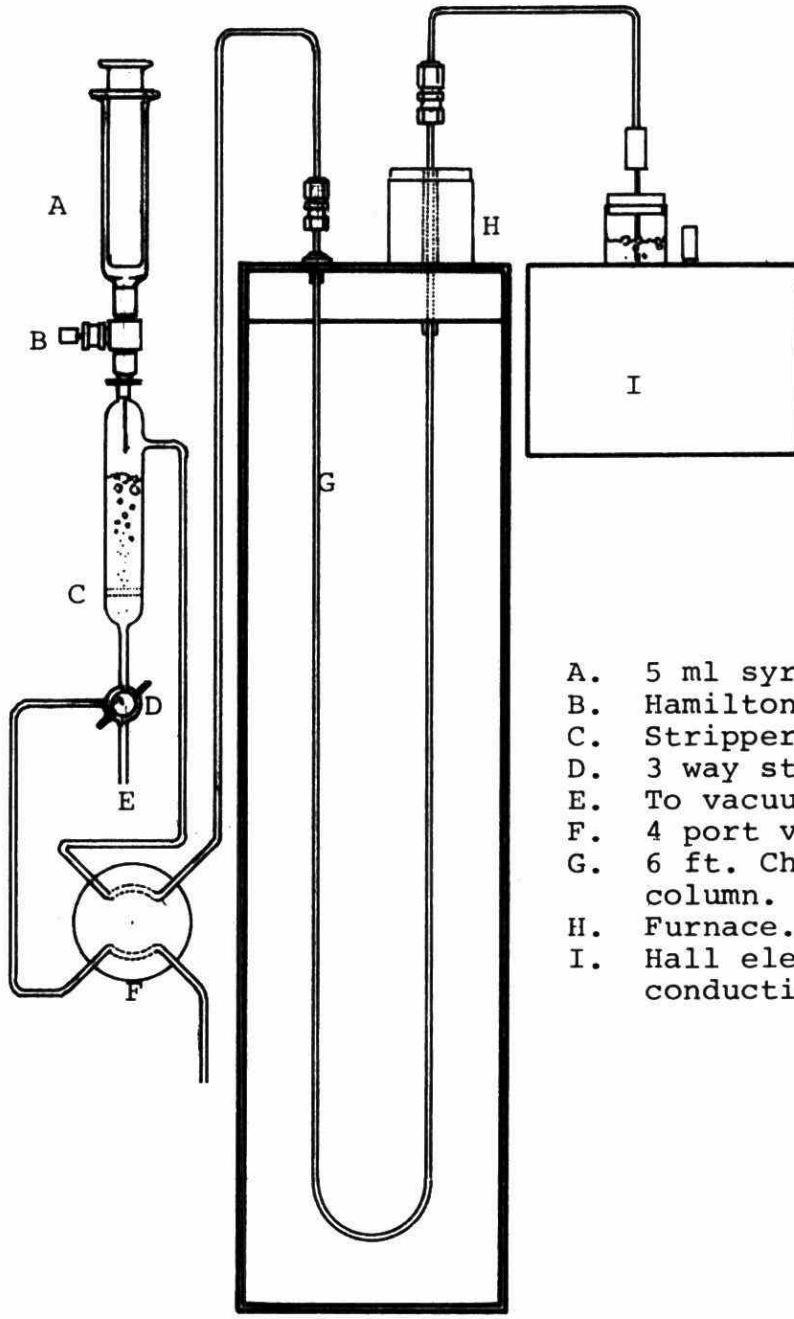
CONDITIONS FOR THE GAS CHROMATOGRAPHIC ANALYSIS OF HALOFORMS USING THE DIRECT AQUEOUS INJECTION TECHNIQUE

INSTRUMENT	Varian 1400
COLUMN	
length	6 ft.
internal diameter	2 mm.
material	glass
packing	Chromosorb 101
DETECTOR	electron capture
TEMPERATURE	
column	150 & 170°C
injector	250°C
detector	250°C
CARRIER GAS, FLOW RATE	N_2, 30 ml/min.

FIGURE 2.


Varian 1400 gas chromatograph
6 ft. x ¼"
Chromosorb W
Scandium
Tritide
Detector
Varian
model 8000
Auto Sampler.
Recorder
Autolab System IVB
Integrator.

SLIDE 3.



A. 5 ml syringe
B. Hamilton 2 way valve
C. Stripper.
D. 3 way stopcock
E. To vacuum.
F. 4 port valve.
G. 6 ft. Chromosorb 101 column.
H. Furnace.
I. Hall electrolytic conductivity detector.

FIGURE 4.

CONDITIONS FOR THE GAS CHROMATOGRAPHIC ANALYSIS OF HALOFORMS USING THE GAS STRIPPING TECHNIQUE.

INSTRUMENT	Varian 2100
COLUMN	
length	6 ft.
internal diameter	2 mm.
material	glass
packing	Chromosorb 101
DETECTOR	Hall Electrolytic Conductivity Detector
hydrogen flow	70 ml/min.
furnace temperature	800°C
TEMPERATURES	
column	35 to 100°C at 20°/min.,100 to 200° at 4°C/min.
detector block	250°C
injector block	room temp.
CARRIER GAS, FLOW RATE	He,30 ml/min.

FIGURE 5.

COMPARISON OF GAS STRIPPING AND DIRECT AQUEOUS INJECTION TECHNIQUES.

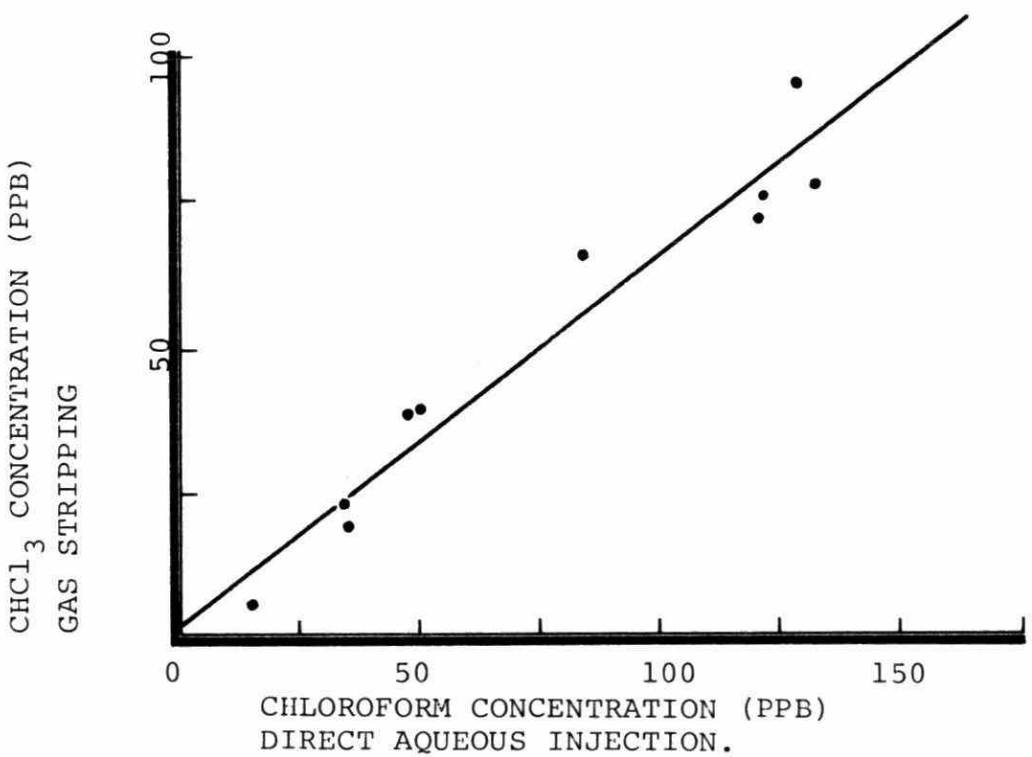


FIGURE 6.

EFFECT OF PURGING ON CHLOROFORM CONCENTRATION

LOCATION	$CHCl_3$ CONCENTRATION (UG/L)		$CHCl_3$ CONCENTRATION (UG/L) AFTER 30 MIN. PURGE.	
	DIRECT AQUEOUS INJECTION	GAS STRIPPING	DIRECT AQUEOUS INJECTION	GAS STRIPPING
CAYUGA, ONT.	129	63	65	3
CAYUGA, ONT.	119	61	60	3
GRAND BEND	28	24	3	0
UNION WTP	13	9	4	0
ELGIN, ONT.	20	18	2	0

FIGURE 7.

EFFECT OF PURGING ON BROMODICHLOROMETHANE CONCENTRATION

LOCATION	$CHCl_2Br$ CONCENTRATION (UG/L)		$CHCl_2Br$ CONCENTRATION (UG/L) AFTER 30 MIN. PURGE.	
	DIRECT AQUEOUS INJECTION	GAS STRIPPING	DIRECT AQUEOUS INJECTION	GAS STRIPPING
ELGIN WTP	10	7	2	0
UNION WTP	10	8	1	0
WINDSOR WTP	13	12	1	0
AMHERSTBURG	12	12	1	0

FIGURE 8.

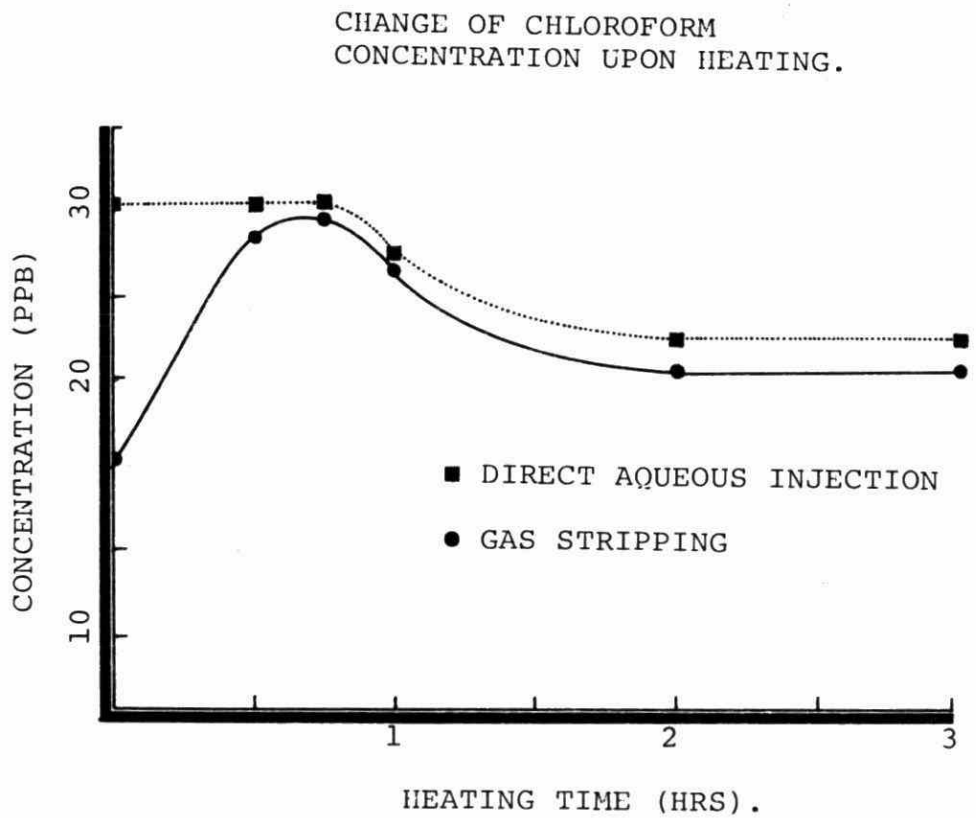

CHANGE OF CHLOROFORM
CONCENTRATION UPON HEATING.
CONCENTRATION (PPB)
10
20
30
1
2
3
DIRECT AQUEOUS INJECTION
GAS STRIPPING
HEATING TIME (HRS).

FIGURE 9.

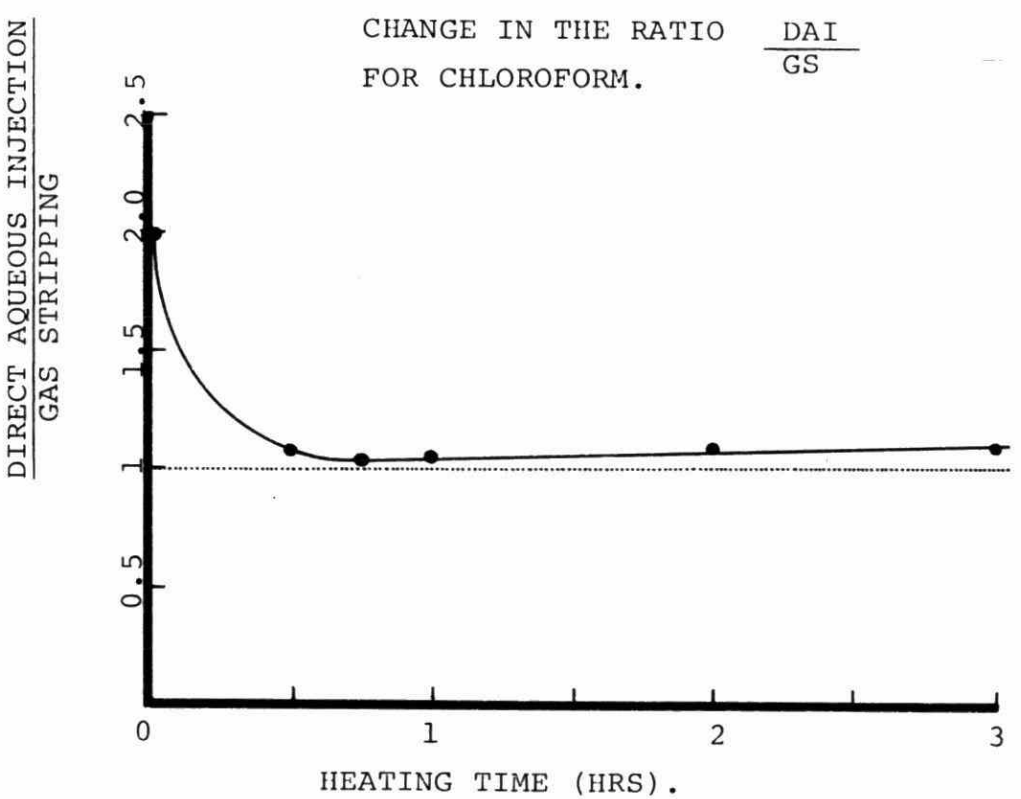

CHANGE IN THE RATIO DAI / GS
FOR CHLOROFORM.
DIRECT AQUEOUS INJECTION / GAS STRIPPING
2.5
2.0
1.5
1
0.5
0
1
2
3
HEATING TIME (HRS).

FIGURE 10.

CHANGE IN THE RATIO $\frac{DAI}{GS}$ FOR BROMODICHLOROMETHANE.

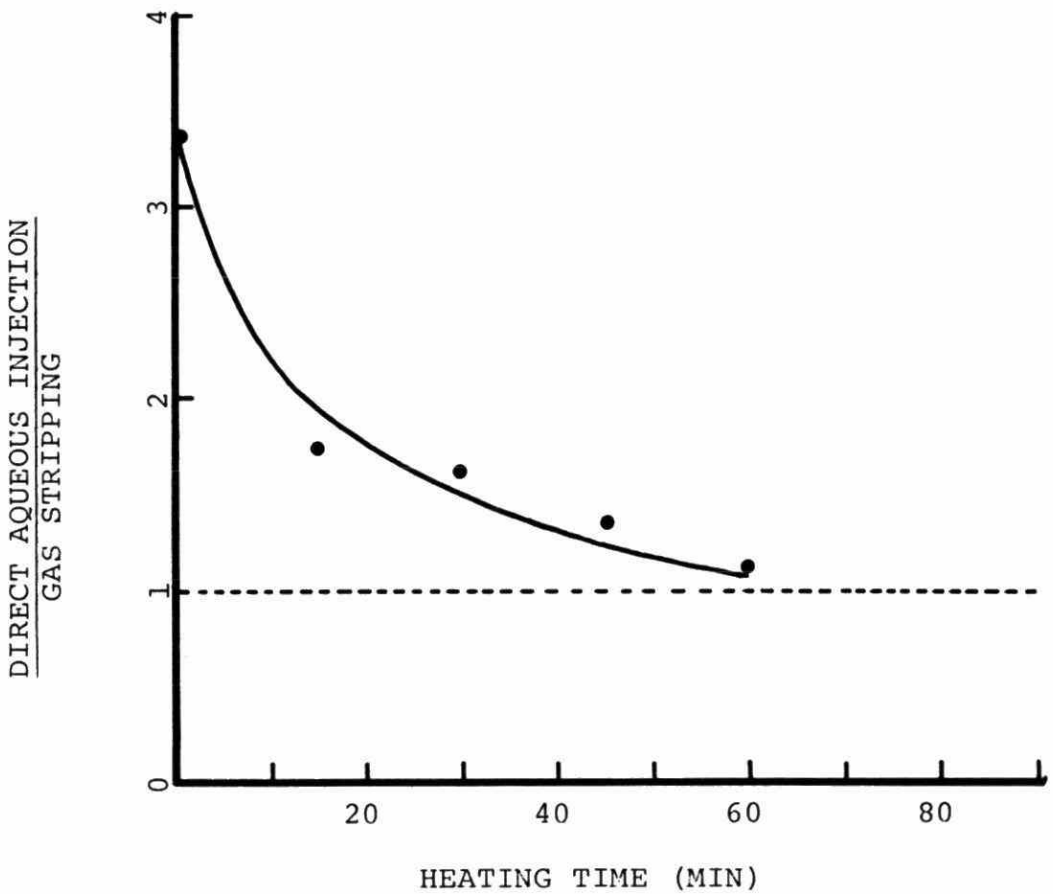


FIGURE 11.

CHLORINATION OF ACETONE

TIME (HRS)	CONCENTRATION OF CHLOROFORM (UG/L) DIRECT AQUEOUS INJECTION	GAS STRIPPING	DAI/GS
1.5	47	31	1.51
2	77	47	1.63
3	126	82	1.53